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EXCITATION AND DEEXCITATION OF VIBRATION IN N_2 BY OXYGEN ATOMS

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SYNOPSIS

The earth's upper atmosphere continuously emits infrared radiation.
It has been suggested that some of this radiation is powered by the energy
stored in vibrationally excited nitrogen and that this is produced when
nitrogen quenches $O(^1D)$. In this reaction the 1.96 eV electronic excita-
tion of $O(^1D)$ is transferred to vibrational and rotational energy of the
nitrogen and kinetic energy. However, no measurements of the fraction
which appears as vibrational energy have been made. One of the tasks of
the current program will be to determine this fraction using Raman spec-
troscopy to determine the populations of the vibrational levels of nitro-
gen that are produced. The apparatus is about complete and preliminary
measurements will soon begin.

Once produced, the vibrationally excited nitrogen is deexcited only
by collisions, among which are those that transfer the energy to hetero-
nuclear molecules which radiate in the infrared. In the E-region of the
earth's atmosphere, however, deexcitation of $N_2(vib)$ will probably be
dominated by collisional quenching by electrons in the lower E-region and
vibrational-translational energy exchange with $O(^3P)$ in the upper E-region.
The reaction rate for the latter process is not known for temperatures
found in the earth's atmosphere. This will be determined in a second task
which will use shock tube and laser schlieren techniques to monitor post-
shock relaxation processes. The shock tube is now fully instrumented,
and preliminary measurements are underway.

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We intend to keep in close touch with theoretical approaches to
these problems. Dr. Fisher of Wayne State University has recently com-
pleted calculations on the $O(^1D)-N_2$ system and obtained a very low (3%)
conversion of the $O(^1D)$ energy to $N_2(vib)$ energy. Its implications for
this program are discussed.

INTRODUCTION

Three years ago[1] it was suggested that the vibrational temperature of nitrogen in the E-region may be considerably higher than the kinetic temperature--a vibrational temperature of about $3100°F$ being postulated. The vibrationally excited nitrogen is deexcited only by collisions, among which are those that transfer the energy to heteronuclear molecules which radiate in the infrared. Processes that excite or deexcite $N_2(vib)$ are thus of particular interest in connection with some defense problems concerned with atmospheric infrared measurements. One of the most important excitation mechanisms may be the quenching of $O(^1D)$ by N_2. The room temperature rate coefficient is very large, but how the energy is partitioned between vibrational, rotational, and kinetic energy has not yet been measured. The most important deexcitation mechanisms are probably collisional quenching by electrons in the lower E-region and vibrational-translational energy exchange with $O(^3P)$ in the upper E-region. Reaction rates for the latter process are not known for temperatures found in the earth's atmosphere. The research program we have started is addressed to these problems and is divided into three tasks. The first of these is to study the production of $N_2(vib)$ when N_2 quenches $O(^1D)$ by using Raman spectroscopy to measure the vibrational state populations. A second task will be to measure the rate of the deexcitation of $N_2(vib)$ by $O(^2P)$ using a shock-tube experiment. A simple model for both these reactions involves potential curve crossings. E. R. Fisher of Wayne State University is currently examining such a model. The third task will provide theoretical support, keeping in close touch with this and other developments.

RESEARCH PROGRAM AND PLAN

Task I Vibrational Population Measurements

The reaction

$$N_2(v=o) + O(^1D) \rightarrow N_2(v=n) + O(^3P) + \Delta E \quad , \quad (1)$$
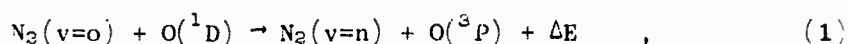
where ΔE is the energy in rotational and translational modes, has been
studied at room temperature in this laboratory[2] as well as others.[3-9]
A rate coefficient for quenching $O(^1D)$ of approximately 5×10^{-11} cm^3
$molecule^{-1}$ sec^{-1} was deduced from our experiment, which not only agrees
with the most recent measurement[8] but is in excellent agreement with the
value deduced from dayglow observations.[10]

None of the laboratory studies has provided any information on the
fraction of the ^1D excitation energy (1.96 eV) which is converted into
vibrational energy of the nitrogen molecule by the quenching reaction.
Similar experiments[11-14] on the quenching of excited mercury atoms by
CO and NO indicate that this fraction may be substantial. (However, see
page 18.) Energetically, the quenching reaction (1) may produce nitrogen
in any level up to n = 7. It is expected[15-22] that the initial vibra-
tional distribution will be rapidly degraded by vibrational exchange
collisions of the type

$$N_2(v=n) + N_2(v=o) \rightarrow N_2(v=n') + N_2(v=n-n') \quad (2)$$

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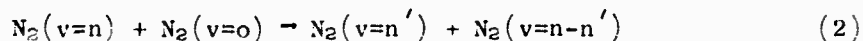
or, effectively,

$$N_2(v=n) + (n-1)N_2(v=o) \rightarrow n\ N_2(v=1) \qquad (2')$$

to produce a non-Boltzmann population of $N_2(v=1)$. Hence, although we shall attempt to measure the concentration of $N_2(v=n)$ as a function of time for each value of $n \leq 7$ and thus deduce separate rate coefficients for each value of $v = n$ in reaction (1), the rapid rate of reaction (2) may make this impossible. It should be possible, however, to measure $N_2(v=1)$ and hence to determine the fraction of ^1D excitation energy which appears as vibrational energy. These measurements will be made by observing Raman scattering of 4880-$\mathring{A}$ Ar^+ laser radiation. The intensity of Anti-Stokes transitions will be measured because these spectra are free from transitions due to the $N_2(v=o)$ level [whereas the Stokes transitions from $N_2(1 \leq v \leq 7)$ lie in the rotational structure of the Stokes lines from $N_2(v=o)$].

Because we use photodissociation of O_2 with a Xe resonance lamp $(1470\mathring{A})$ to produce $O(^1D)$ and $O(^3P)$, the atoms carry 0.7 eV of translational energy. We can, therefore, by adding an inert buffering gas, study reaction (1) over the range of energies, or equivalent temperatures, found in the earth's atmosphere (up to $1500^{\circ}K$).

Removal of $N_2(v=1)$ will be by gas flow from the cell, deactivation on the cell walls, quenching by impurities, or by

$$N_2(v=1) + O_2(v=o) \rightarrow N_2(v=o) + O_2(v=1) \qquad (3)$$

or

$$N_2(v=1) + O(^3P) \rightarrow N_2(v=o) + O(^3P) \qquad (4)$$

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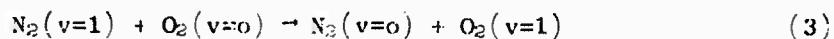
Information on these rates will be obtained by pulsing the Xe resonance lamp and observing the decay of the signal from $N_2(v=1)$. The measurements will be used to establish rate coefficients for (3) and (4) (or at least upper limits if they cannot be made rate controlling). The measurements will be made at temperatures up to $\sim450^{\circ}K$ (a limit imposed by our experimental design). At temperatures much above $450^{\circ}K$ the thermal population of $N_2(v=1)$ would, in any case, limit or prevent the measurement of its deactivation rate.

Task II   Deexcitation of $N_2(v=1)$ by $O(^3P)$

In Task II the rate of the reverse of reaction (4), from which the direct rate of (4) can be obtained, will be measured by shock tube techniques. The results of Breshears and Bird[23] above $3000^{\circ}K$ will be confirmed and extended as far as possible to lower temperatures.

Task III   Theory

The fact that $O(^3P)$ is approximately ten times more effective than O_2 in relaxing $N_2(vib)$[23] is related to the nature of the potential energy curves for N_2O. Crossings between these curves are probably responsible for the quenching of $O(^1D)$ by N_2, for the deactivation of $N_2(vib)$ by $O(^3P)$, and for the thermal and photodissociation of N_2O. For the N_2O dissociation there are many data,[24] and some controversy exists about the height of the lowest crossing point. An interpolation scheme for reaction (4) as a function of T should be consistent with the other information available. A simple model including potential curve crossings appears to be a likely basis for such a scheme. E. R. Fischer of Wayne State University is currently examining such a model, and we are keeping in close touch with this and other developments.

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ACCOMPLISHMENTS

Task I   Vibrational Population Measurements

Experimental

The vibrationally excited nitrogen will be produced by photolysis
of a mixture of oxygen and nitrogen at 1470 Å. In this mixture the
$O(^1D)$ produced by photodissociation of the oxygen can be quenched by
nitrogen (reaction 1). The concentration of the vibrationally excited
nitrogen which results will be determined by measuring the intensity
of Raman scattering from a focused beam of 4880-Å Ar^+ laser radiation.
Cross sections for Raman scattering by vibrationally excited nitrogen
have been calculated, enabling concentrations to be calculated from the
observed intensities.

The experimental arrangement is shown in Fig. 1. It consists of
several major components. The nucleus of the experiment is the cell
in wnich the oxygen-nitrogen mixture is irradiated with 1470-Å light.
The output of an Ar⁻ ion laser traverses this cell and is focused to a
point within the cell. This focal point is then imaged on the slit of
a spectrometer by a second optical system. The light passing through
the exit slit of this spectrometer is imaged on the photocathode of a
photomultiplier. Its output is measured in a pulse-counting system
and stored in the memory of a C.A.T. (Computer of Average Transients).
Coherence between the channels of the C.A.T. and the wavelength setting
of the spectrometer will be obtained by using a controller to advance
both channels in the C.A.T. and the wavelength drive on the spectrometer.
This will enable repetitive scanning and signal integration to be carried
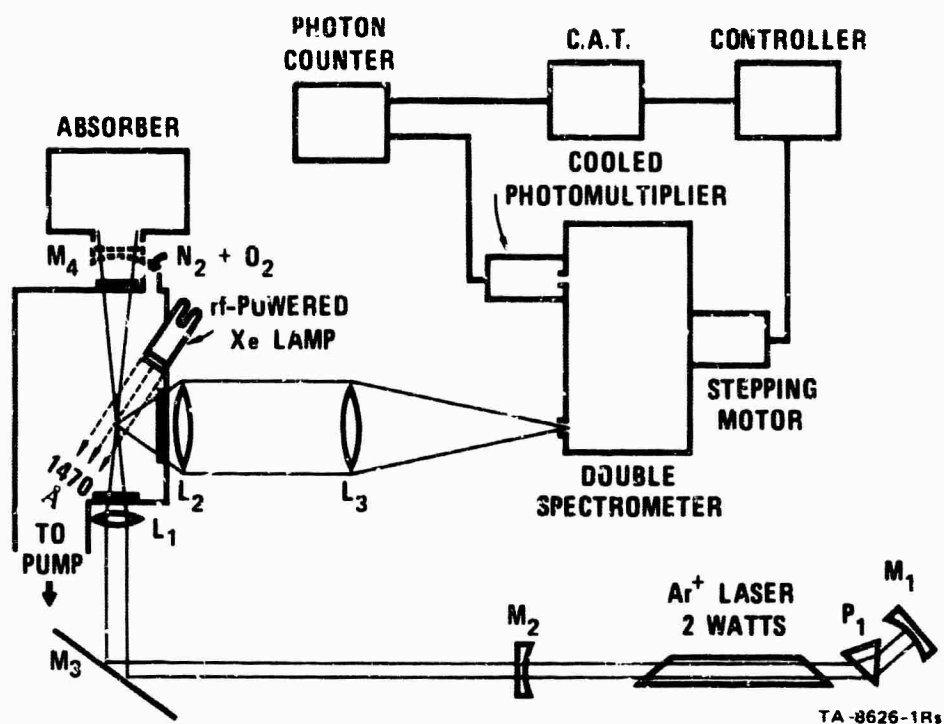out for long periods of time.

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FIGURE 1   EXPERIMENTAL ARRANGEMENT FOR RAMAN SPECTROSCOPY.
The lens L_2, which has an aperture ratio of f/0.95 and a focal length of
5.0 cm, collects the Raman-scattered light over a large solid angle.

The spectrometer is a Spex Model 1402 double spectrometer equipped
with an FW 130 photomultiplier tube in a thermoelectrically cooled
housing. A Fluke high voltage power supply (Model 412B) provides the
photomultiplier voltage. The photomultiplier output is amplified and
discriminated by an SSR Model 1120 photon counter before being fed to
an Ortec gate and delay generator (Model 416A). The stretched output
of this unit is then coupled to a Canberra Model 1480 linear ratemeter
for counting. The stretched output of the Ortec Model 416A is compatible
with the input of a Technical Measurement Corporation's Computer of
Average Transients (C.A.T. Model 1000). The controller, which is used
to synchronize the integration time/channel of the C.A.T. and the stepping
rate of the motor of the spectrometer, is presently being constructed
using Digital Equipment Logic Modules. The photon-counting system is

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operational, and the conditions for photon counting with the FW 130 have been ascertained.

The laser is an argon-ion laser (Coherent Radiation Laboratories Model 52A) equipped for single wavelength selection and providing 700 mW CW at 4880 Å. Mirror M_3 reflects the laser beam through 90° so that the Raman light can be focused on (and not across) the spectrometer slit. To enhance the power density of the laser radiation, an antireflection-coated lens L_1 of focal length 3 in. (one of 4-3/4 in. is also available) converges the beam to a focus in the region that is the image of the spectrometer slit as formed by lenses L_2 and L_3. The lens L_2 is an f/0.95 Angenieux with a focal length of 5.0 cm. The lens L_3, an f/5.6 Carl Meyer Tele lens with a focal length of 16 in., was chosen so as to fill the acceptance cone of the spectrometer. If necessary, a further increase in the power density may be achieved by using a mirror M_4 to return the transmitted beam back through the cell. Lenses L_1 and L_2 are mounted in positioners (Gaertner Scientific No. R287) allowing motion in three mutually perpendicular directions. When mounts for M_3 and L_3 are completed, all the optical components will be mounted on an optical bench which is attached to the front of the spectrometer. All the equipment is on a vibration-free concrete table.

The rf-powered Xe resonance lamp (Fig. 1) is a standard item of equipment in this laboratory and has been in use for several years.[25-27] It incorporates a sapphire window connected to the lamp body through a graded seal, is filled with ~1 torr Xe, and has a Ba-Al-Ni getter to maintain gas purity. It can be operated in either a continuous or pulsed mode with an intensity of ~3 $\times$ 10^{15} quanta/sec in the resonance line. The visible emission from this lamp is particularly rich in blue light, which is the wavelength region in which we will observe the anti-Stokes Raman lines of N_2(vib). Hence the cell is being designed to minimize scattered light from the Xe lamp.

Initial experiments will be carried out by blowing air into the focal region of the lens L_1 for, as Table I shows, the pressure of $N_2(v=1)$ in air provides a very convenient means of determining the sensitivity of our apparatus for this species. If no delays had been

Table I

PRESSURE OF $N_2(v=1)$ IN AIR AT VARIOUS TEMPERATURES

Temperature $^\circ$C	$[N_2(v=1)]/[N_2(v=0)]$	$[N_2(v=1)]$ torr in air at 760 torr
-50	2.96×10^{-7}	1.76×10^{-4}
-30	1.02×10^{-6}	6.05×10^{-4}
-10	2.91×10^{-6}	1.73×10^{-3}
5	5.79×10^{-6}	3.44×10^{-3}
27	1.40×10^{-5}	8.31×10^{-3}
50	3.11×10^{-5}	1.85×10^{-2}

encountered, these preliminary experiments with air would have been in progress, if not completed, at this time. A three-month delay in delivery of the double spectrometer and its accessories by Spex Industries of Metuchen, New Jersey, has, however, prevented this (the final item was delivered one month ago). An increased rate of effort during the remainder of the contract period should compensate for some, and possibly all, of this delay. The situation will be clearer in three months' time when a more meaningful assessment can be made (which will be included in the next report).

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Theory of Task I

The experiment is to measure the $N_2(\text{vib})$ [produced when nitrogen quenches $O(^1D)$] by Raman scattering of a laser beam. Three major factors enter into a calculation of the feasibility of this approach: the concentration of $N_2(\text{vib})$ that will be present, its cross section for Raman scattering, and the sensitivity of an optical system for measuring this scattering. These factors are discussed separately in the following sections.

1. Vibrationally Excited Nitrogen Concentration

The concentration $[N_2(\text{vib})]$ will be governed by

$$[N_2(\text{vib})] = \frac{P}{Q} \tag{5}$$

where P is the production rate of $N_2(\text{vib})$ and Q is the rate at which $N_2(\text{vib})$ is removed from the system.

Since the success of the experiment hinges on obtaining as high a concentration of $N_2(\text{vib})$ as possible, we should carry out the experiment in such a way as to maximize P and minimize Q. The former consideration suggests that experiments be performed with enough oxygen to absorb essentially all the 1470-Å light (say ~1 torr for a path length of 10 cm) and a sufficiently higher pressure of nitrogen so that the major loss of $O(^1D)$ is by reaction (1) and not by

$$O(^1D) + O_2 \rightarrow O_2(b^1\Sigma_g^+) + O(^3P) \quad . \tag{6}$$

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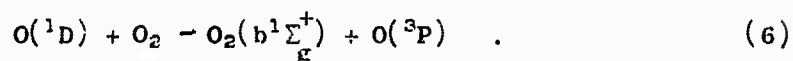
This requires[28] $p_{N_2} > 10 p_{O_2}$. Under these conditions and assuming reaction (2) follows reaction (1),

$$p_{N_2(v=1)} = 7 \frac{If}{V} \tag{7}$$

where

   I = Xe lamp intensity (photons/sec)

   f = the fraction of the $O(^1D)$ energy that is converted to vibrational energy in N_2

   V = volume of the cell

and the factor 7 is introduced because each $O(^1D)$ has enough electronic energy to produce up to 7 molecules in $N_2(v=1)$.

In our experiment, $N_2(v=1)$ will be removed by both chemical and physical processes. The rate expression is

$$Q_{N_2(v=1)} = k_3[O_2] + k_4[O] + k_M[M] + \frac{1}{\tau_D} + \frac{1}{\tau_P} \tag{8}$$

where $k_M[M]$ represents impurity quenching and τ_D and τ_P are the diffusion and pumpout times of $N_2(v=1)$.

In order to decide how to minimize Q and hence maximize the concentration $[N_2(v=1)]$ we must first decide which of the terms in the above expression will be of most importance. We can show that diffusion will probably be controlling by the following simple treatment.

The diffusion time τ_D is given by

$$\tau_D = \left(\frac{R^2}{15d}\right) p + \frac{4R}{3\bar{v}\ \gamma} \tag{9}$$

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where R is the radius of a supposedly spherical container, γ is the catalytic efficiency of the bounding surfaces, $\bar{v}$ is the mean thermal velocity of $N_2(v=1)$, d is the diffusion coefficient of $N_2(v=1)$ at 1 torr, and p is the pressure (torr). No measurements of γ for $N_2(v=1)$ are available, but an assumption of $\leq 10^{-4}$ would give $\tau_D \geq 1$ sec. If $\gamma > 10^{-4}$, then this same value of τ_D can be obtained by using a high pressure of buffering gas, such as He or Ar (in this case the value of τ_D is dominated by the first term in Eq. 9). For a static or slow-flowing system ($\tau_p > 1$ sec) diffusion will therefore dominate gas flow as the major physical process removing $N_2(v=1)$. But how does this rate compare with the rate of the chemical processes? For pure gases ($[M] \sim [O]$) the chemical processes will be dominated by quenching with molecular oxygen (since $[O]$ will be approximately $10^{-4}[O_2]$ in our cell) and we can use a very long extrapolation of the data of Breshears and Bird[23] to obtain, for 1 torr oxygen at room temperature, $k_3[O_2] \sim 10^{-2}$ sec^{-1}. Hence, at room temperature, diffusion will dominate the other terms in Eq. (8) and we can write $Q_{N_2(v=1)} \leq 1$ sec^{-1}.

Using this value of Q and Eq. (7) for P with $I = 3 \times 10^{15}$ quanta/sec, $V = 1000$ cm^3 and $f = 1$, substitution in Eq. (5) gives the concentration $[N_2(v=1)] \geq 2.1 \times 10^{13}$ cm^{-3}. As the temperature is increased, $k_3[O_2] + k_4[O] + k_{,i}[M]$ will become greater than $1/\tau_D$ and the concentration $[N_2(v=1)]$ will be reduced. To calculate the Raman signal from this $[N_2(v=1)]$ we must know the cross section. This can be calculated in the manner shown below.

2. Raman Cross Section

For plane-polarized incident light with the E vector perpendicular to the plane of scattering, the differential scattering cross section for the Raman radiation in the Q branch of the vibration-rotation band is given by[28]

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$$\left(\frac{d\sigma}{d\Omega}\right)_{Stokes} = \left(\frac{2\pi}{c}\right)^4 \frac{h(n+1)}{8\pi^2\mu} \frac{(\nu_o-\nu_n)^4}{\nu_n} \left[(\alpha')^2 + \frac{7}{45}(\gamma')^2\chi\right] \qquad (10)$$

and

$$\left(\frac{d\sigma}{d\Omega}\right)_{Anti\text{-}Stokes} = \left(\frac{2\pi}{c}\right)^4 \frac{hn}{8\pi^2\mu} \frac{(\nu_o+\nu_n)^4}{\nu_n} \cdot \left[(\alpha')^2 + \frac{7}{45}(\gamma')^2\chi\right] \qquad (11)$$

where

n is the vibrational level

μ is the reduced mass

ν_o is the radiation frequency

ν_n is the frequency of the Raman-active molecular vibration

$\alpha' = (\partial\alpha/\partial R)_o$ is the polarizability derivative at the equilibrium separation

γ' is the anisotropy of the polarizability derivative

χ is the fraction of anisotropic intensity in the Q branch.

For N_2

$$\nu_1 = 2331 \text{ cm}^{-1}$$
$$\alpha' = 1.75 \times 10^{-18} \text{ cm}^2$$
$$\chi(\gamma'/\alpha')^2 = 1.71$$

so that the cross sections at 4880 Å are

$$(d\sigma/d\Omega)_{Stokes(n=o-1)} = 7.3 \times 10^{-31} \text{ cm}^2/\text{ster} \qquad (12)$$

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and

$$(d\sigma/d\Omega)_{Anti\text{-}Stokes(n=1\rightarrow0)} = 1.8 \times 10^{-30} \text{ cm}^2/\text{ster} \quad . \tag{13}$$

We can use these cross sections to estimate the intensity of
the signal to be expected from a given density of $N_2(n=1)$. However,
for actual measurements, we can use intensity ratio measurements to
eliminate the need for knowledge of absolute collection and detection
efficiencies because

$$\frac{I_{10}}{I_{01}} = \frac{[N_2(v=1)]}{[N_2(v=0)]} \frac{d\sigma}{d\Omega_{10}} \bigg/ \frac{d\sigma}{d\Omega_{01}} = \frac{[N_2(v=1)]}{[N_2(v=0)]} \frac{(\nu_0+\nu_1)^4}{(\nu_0-\nu_1)^4} \quad . \tag{14}$$

Hence

$$[N_2(v=1)] = [N_2(v=0)] \cdot \frac{(\nu_0-\nu_1)^4}{(\nu_0+\nu_1)^4} \cdot \frac{I_{10}}{I_{01}} \tag{15}$$

where the intensity is normalized to the incident beam power and cor-
rected for wavelength dependence of the detection efficiency. The
expected signal from $N_2(v=1)$ can now be estimated in the following
manner.

3. Raman Signal

It can be readily shown that the number of Raman scattered
photons from a small volume V into a collection angle of Ω steradians
is given by

$$N_{Raman} = P\lambda \cdot \frac{\sigma\rho}{M} \cdot \frac{\Omega V}{A} \cdot 3.03 \times 10^{46} \text{ photons sec}^{-1} \tag{16}$$

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where P(watts) is the power, λ(cm) is the wavelength, and A(cm^2) is the beam cross section (at the volume V) of the laser; and σ(cm^2 ster^{-1} molecule^{-1}) is the Raman cross section, ρ(g cm^{-3}) is the density, and M(g mole^{-1}) is the molecular weight of the scatterer.

If an optical system of efficiency η and a detector of quantum efficiency Q is used, the number of counts per second R will be given by

$$R = P\lambda\eta Q \cdot \frac{\sigma\rho}{M} \cdot \frac{\Omega V}{A} \cdot 3.03 \times 10^{46} \text{ photons sec}^{-1} \quad . \tag{17}$$

For a 2-mm laser beam of 4880-Å radiation focused with a 3-in. focal length lens, the simple treatment of Barrett and Adams[29] gives $V = 1.47 \times 10^{-6}$ cm^3 and $A = 4.2 \times 10^{-6}$ cm^2. The count rate can now be estimated using the following values for the other parameters in Eq. (14):

P = 700 mW

$\gamma = 0.488 \times 10^{-4}$ cm

$\sigma = 1.8 \times 10^{-30}$ cm^2 ster^{-1} molecule^{-1}

$\rho = 0.97 \times 10^{-9}$ g cm^{-3}
    [for N$_2$(v=1) $= 2.1 \times 10^{-13}$ cm^{-3}]

M = 28 g mole^{-1}

$\eta = 0.3$

Q = 0.2

$\Omega = 1$ steradian

The estimated count rate at the Q branch of the Anti-Stokes of N$_2$(v=1−0) is then

$$R = 1.4 \text{ counts/sec} \quad . \tag{18}$$

This is to be compared with the 1 count/sec dark current counting rate from our FW 130 PM tube. If necessary, this background can be further reduced by chopping techniques. It is obvious, however, that good signal-to-noise will require long integration times.

Task II Deexcitation of $N_2(v=1)$ by $O(^3P)$

Work on Task II, which involves the measurement in a shock tube of the influence of atomic oxygen on the vibrational relaxation of nitrogen, has been devoted mainly to facility developments up to the present time. The shock tube that existed at the beginning of the project had been used for qualitative testing at atmospheric pressure in air at much higher Mach numbers than are required in this program. In this reporting period, the shock tube has been modified for the quantitative testing at low pressures and Mach numbers as required in this program. A schematic of the apparatus is shown in Fig. 2. A vacuum station has been installed which reduces system pressure below 5 X 10^{-6} torr. The system leak rate is less than 10^{-4} torr/min. A test gas supply has been provided, with pressure gauges covering the range 1 to 100 torr anticipated in the tests. The test section has been fitted with three heat-gauge type shock detectors, and the gauges and required amplifiers have been built. A new diaphragm holder with square cross section has been built, which facilitates the use of scribed diaphragms, and a scribing tool which produces clean, reproducible scribes has been provided. The use of scribed aluminum diaphragms has eliminated all problems of fragmentation. With these improvements, the shock tube itself is complete, although modifications to the test section, described below, may be required.

The optical system required for the laser schlieren measurements is also essentially complete. A Spectra-Physics Model 122 He-Ne laser will be used. Two UDT Model PIN-8LC photodetectors have been procured

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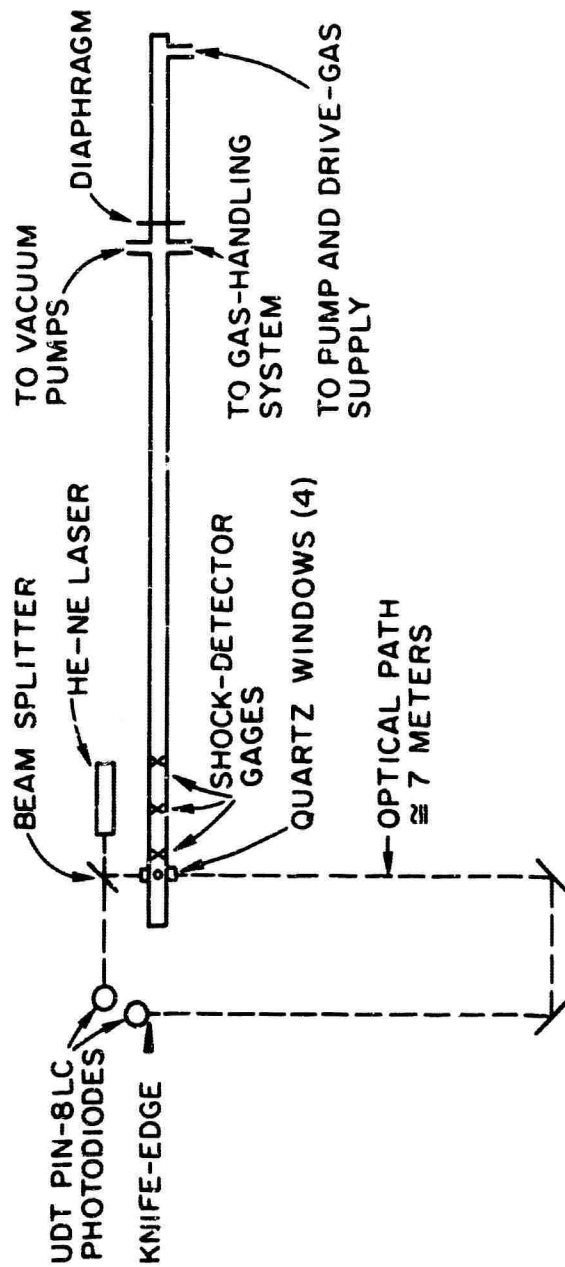
FIGURE 2   EXPERIMENTAL ARRANGEMENT FOR THE SHOCK TUBE MEASUREMENTS. A 2537 Å light source and a RCA 1P28 PM tube monitors the O_3 concentration at right angles to the laser beam.

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and the associated circuitry developed. In addition, preamplifiers,
which may be required in view of the small signal level anticipated in
these tests, have been designed and built.

A series of tests run to check out the performance of the shock
tube and laser schlieren systems indicate that there is a high level
of "noise" in the detected intensity history following passage of the
shock wave. Such fluctuations could result from turbulence in the test
gas or from mechanical vibrations in the optical system. The use of
flat windows in a round test section does result in surface disconti-
nuities, which could readily lead to disturbances in the gas flow.
Optical schlieren studies are now under way in an attempt to verify
this. If it should be necessary to redesign the test section to
eliminate the problem, a delay of one month in the start of testing
could be anticipated.

The present schedule of events required to carry out Task II is
as follows. Testing should begin by 1 January 1971. Twenty-five tests
in pure N_2 will require three weeks, 30 tests in N_2-O_2 mixtures will
require four weeks, and 35 tests in N_2-O_3 mixtures five weeks. Thus
the required data should be taken by 1 April 1971. Data reduction and
analysis, which will be carried out simultaneously with the testing,
can hopefully be completed by 1 August 1971, thus meeting the contract
time limitation. A major redesign of the test section, if required,
might strain this time schedule, however.

Task III Theory

A semiquantitative calculation of the cross section for the quenching
of $O(^1D)$ by N_2 as a function of the final vibrational quantum number of
the nitrogen molecule has been reported recently.[30] The implications
for our measurements were thoroughly discussed with Dr. Fisher when he

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visited us on December 9. I1 the fraction of the $O(^1D)$ energy converted to vibrational energy in N_2 is indeed only 0.03, then the expected signal will be reduced by a factor of 33. A positive measurement of so small a signal may be very difficult, if not impossible, with the present equipment. A fuller assessment of the implications of this calculation will be possible when both the apparatus sensitivity for $N_2(v=1)$ and the lifetime of $N_2(v=1)$ in a pyrex cell have been determined. If the measurement turns out to give a null result within the sensitivity available, this conclusion, while less gratifying t the scientist, may provide a very significant validation of the theory and a very significant piece of information with regard to the practical consequences in upper atmosphere reactions. To be sure, confidence in such a null measurement requires a particularly careful evaluation of the limits of error in the experiment.

In the course of our discussions with Dr. Fisher, we considered also other methods of testing the theoretical calculations. In particular, since part of his theoretical model involves the interactions that are responsible for vibrational excitation and deexcitation of N_2 by ground-state O atoms, his theory is car le of predicting the vibrational relaxation rate as a function of temperature. Such a prediction could be tested at present against the data of Breshears and Bird[23] and also against the information we hope to obtain at lower temperatures in our own shock-tube measurements in Task II. Other possible predictions o1 the theory, including predissociation in N_2O, were also suggested.

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